DETERGENT FORMULATIONS BASED ON AMPHOTERIC SURFACTANTS AND SOAP
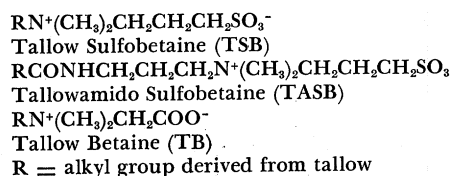
Introduction

In recent years, the Eastern Regional Research Center has carried out an extensive study of soap-based detergents. The underlying principle of this research was developed by Bistline and coworkers (1). They found that a three-component system consisting of tallow soap as the major ingredient, a lime soap dispersing agent (lsda), and an inorganic builder, typically a glassy sodium silicate, could be formulated into a detergent which performed as well as a typical phosphate-built detergent. These soap-based detergents were effective in hard water; however, the composition had to be held within certain ratios in order to achieve maximum detergency. Details of formulation of such a system were described by Noble and coworkers (2).

A great variety of anionic surfactants was found to be effective as lsda. Originally, fat derivatives were studied such as α-sulfonated fatty esters (3), sulfated fatty alkanolamides (4), sulfopropylated fatty alcohols, fatty acids or fatty amides (5), or sulfopropylated fatty derivatives of iminodiacetic acid (6). Later, this study was extended to anionic lsda derived from alkylbenzenes, such as sulfonated or sulfated sulfonamides (7) or sulfonated esters of alkylaroylpropionic acids (8), all of which were found to be effective lsda which could be formulated into soap-based detergents of high detergency performance. It was recognized by Stirton and coworkers (9) that the presence of a large hydrophilic bulk in a surfactant molecule was essential for good lime soap dispersing properties, and it was therefore assumed that nonionic surfactants would be outstanding lsda. Nonionics indeed proved to be outstanding lsda; however, soap-nonionic formulations failed to give acceptable detergency (10).

Amphoteric surfactant molecules also possess a large hydrophilic bulk, so that it would appear that such surfactants might also show promise as lsda in soap-based detergent formulations. Linfield and coworkers (11) showed that certain fat-derived sulfobetaines and sulfated quaternary ammonium compounds were compatible with soap with respect to detergency, while Hirst (12) showed that some surface-active sulfobetaines of petrochemical origin were also useful as lime soap dispersing agents.

In the present study we investigated the detergency characteristics of three tallow-derived amphoteric surfactants. Since the proper chemical names for the compounds are rather complex, we adopted a simplified nomenclature and abbreviated code as follows:

$RN^+(CH_3)_2CH_2CH_2CH_2SO_3^-$
Tallow Sulfobetaine (TSB)
$RCONHCH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3$
Tallowamido Sulfobetaine (TASB)
$RN^+(CH_3)_2CH_2COO^-$
Tallow Betaine (TB)
R = alkyl group derived from tallow

Ernst (13) obtained a patent on the two types of sulfobetaines. The synthesis of a homologous series of pure compounds of the two types of sulfobetaines and their physical and surface-active properties were described in a recent paper by Parris and coworkers (14). Therefore, in the subsequent sections the synthetic approaches are not discussed in great detail. Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Synthesis of TSB

A solution of 150 g (0.52 mole) N,N-dimethyl tallowamine (Armeen DMHTD) in 300 ml 1,2-dichloroethane was heated to 50°C and 64.0 g (0.52 mole) of propanesultone was added drop-wise with stirring over a 40 minute period. Occasional cooling was required to maintain the temperature at 50°C, since the reaction was exothermic. Thereafter, the reaction mixture was refluxed for a period of 30 minutes. The mixture was cooled to 40°C and the product precipitated with 400 ml acetone. The resulting white crystalline precipitate of crude sulfobetaine was filtered off at room temperature. A 94 percent yield was obtained. The product was used for subsequent evaluations without further purification.

Synthesis of TASB

To 1200 g (1.40 mole) melted whole tallow, 460 g (4.49 mole) N,N-dimethyl-1,3-propanediamine was added with stirring. The reaction flask was stoppered and allowed to stand at room temperature for two days at which time approximately 90 mole percent amide was indicated by infrared absorbance. One liter 1,2-dichloroethane was added to the amide after the unreacted diamine had been removed by evaporation for six hours at 65°C/0.15 mm. The reaction mass was heated to 50°C and 524 g (4.29 mole) propanesultone was added dropwise over a one-hour period with cooling in order to maintain the temperature at about 50°C. Thereafter, the mixture was kept at 50°C for one hour. Since the product precipitated out as an amorphous lumpy mass, heat had to be applied to keep the reaction mass fluid. The solvent was removed in a vacuum oven, leaving behind a quantitative yield of slightly tacky, solid product which was used for detergency testing without purification.

It should be noted that the crude TASB contained all of the glycerol obtained as a by-product of the first step of the synthesis. The glycerol was left in the product because its presence helped to dissolve the rather insoluble TASB in water. Furthermore, the removal of glycerol would have added a cumbersome processing step to the synthesis.

Synthesis of TB

To 200 ml isopropyl alcohol containing 33.0 g (0.35 mole) chloroacetic acid was added 100 g (0.35 mole) N,N-dimethyl tallowamine (Armeen DMHTD) followed by 19.4 ml (0.349 mole) 18 N sodium hydroxide. The reaction mass was refluxed for two hours, and the sodium chloride which precipitated was removed by filtration at room temperature. The solvent was removed on a rotary evaporator, and the dry product was again taken up in 200 ml isopropyl alcohol to remove residual insoluble sodium chloride by filtration. The dry product was obtained in a nearly quantitative yield as a white amorphous solid. It was used in subsequent evaluations without further purification.

Formulations and Detergency Evaluations

In previous publications from this laboratory (1, 2) optimized formulations for a tallow soap-anionic lsda-glassy silicate detergent system had been worked out. It was anticipated, however, that amphoteric lsda would follow a somewhat different pattern. Accordingly, soap-lsda blends were prepared in ratios of 90:10, 85:15, 80:20, 75:25, and 70:30. To these soap-lsda blends, we added 10, 15, 20, 30, 40, and 50 percent sodium silicate, respectively. Various types of silicates were used whose Na_2O/SiO_2 ratios were 1/1, 1/1.6, 1/2.0, and 1/2.4, respectively. Thus a total of 120 formulations were prepared. The resulting formulations were then subjected to single wash screening tests in a Tergotometer at 120°F and 300 ppm water hardness. Three commercial soiled cloths were used, EMPA 101 cotton (EMPA), U.S. Testing cotton (UST), and Testfabrics polyester-cotton blend with permanent press finish (TF). The three types of soiled cloth

were washed together in the same beaker as previously described (2); the detergency (ΔR) was measured in terms of increase in reflectance after washing. In this test series and all subsequent ones, 1 percent of sodium carboxymethylcellulose (CMC) was added to each formulation to act as a soil antiredeposition agent. Two leading commercial detergents were used as a control in the detergency tests. Control A is a phosphate-built anionic detergent. Control B is a carbonate-built anionic detergent. Both are sold under the same brand name.

In contrast to the formulation studies reported previously (1, 2) with anionic lsda, the formulations containing an amphoteric lsda were surprisingly unaffected by changes in the relative amount of each component. This is shown in Table I, which is a summary of the detergency tests carried out with the TSB amphoteric surfactant. Since sodium silicates having $Na_2O:SiO_2$ ratios varying from 1:1.6 to 1:2.4, when incorporated into the detergent formulations, gave essentially the same detergency results, only the data obtained with the 1:1.6 $Na_2O:SiO_2$ silicate are given in the table. The ΔR values given represent the spread of readings observed when from 10 to 50 percent of a 1:1.6 $Na_2O:SiO_2$ sodium silicate was added. The addition of silicate to the formulation did not have a dramatic effect on the detergency, and there was no good correlation between the level of silicate added and the ΔR values. In fact the observed range of ΔR readings is frequently only slightly larger than the previously established standard deviation for the three test cloths (1). It was also found, however, that sodium metasilicate gave slightly inferior results. Since the use of metasilicate might pose a safety hazard, it would seem advisable not to use it in household detergents anyhow. Since soap can hydrolyze and fatty acid may be formed in neutral or slightly acidic tap water, a slightly more alkaline grade of silicate such as 1:1.6 or 1:2.0 is recommended over the 1:2.4 grade commonly used by the detergent industry. As far as the amount of silicate to be added to a soap-sulfobetaine mixture is concerned, it can be concluded that the level of added silicate is largely a matter of economics. As long as tallow soap and lsda are more expensive than silicate, it would be advisable to incorporate a high level of silicate into the formulation.

The ratio of soap:lsda likewise had a less dramatic effect than observed previously for the anionic lsda. A slight detergency maximum could be observed for the 80:20 and 75:25 soap:lsda ratios. The ΔR values in this region are equal or very close to those of Control A, a leading commercial phosphate-built detergent. Since analogous data obtained with TASB were very similar to those obtained with TSB, they are not shown here.

Conceivably this substantial latitude in formulation with the two sulfobetaines was due to their outstanding lime soap dispersing properties. This property is measured according to the method of Borghetty and Bergman (15) which gives the amount of lime soap dispersant required to keep 100 g of sodium oleate dissolved in hard water. The lime soap dispersant requirements (lsdr) of the amphoterics as well as those of some anionic surfactants are listed in Table II. The lsdr values of 3 for TSB and TASB are about the lowest observed for any type of surfactant. The alkylbetaine TB gave a surprisingly low value of 12 but, as will be shown below, it did not do well in detergency tests. Linear alkylbenzene sulfonate (LAS) with a value of 45 and a C_{16} α-olefin sulfonate (AOS) with a value of 25 provide quite a contrast to the amphoteric compounds. Sodium methyl α-sulfotallowate (TMS) which was used as the lsda of choice in much of the previous research on soap-based detergents (1, 2) gave a value of 9. While it is recognized that there is no direct correlation between lsdr and detergency, it has become apparent that the performance of an lsda in soap-based detergents hinges upon a low lsdr, a high degree of compatibility with soap and good detergency of the lsda by itself. TSB and TASB fulfill all three criteria.

In view of the high cost of an amphoteric lsda, it was important to determine whether soap-amphoteric surfactant-silicate formulations could tolerate the addition of sodium sulfate.

In a second series of single-wash experiments, the three betaine formulations were evaluated for detergency with and without added sodium sulfate. The results are shown in Table III. The betaine TB was shown to be inferior to TSB or TASB. However, considering the fact that carboxylic acids or their salts usually are poor lsda, the betaine TB did not do as poorly as might be anticipated. TASB and TSB show a fairly consistent detergency pattern. In both cases EMPA and TF detergency decreases as the amount of sodium sulfate is increased whereas UST cotton detergency remains unaffected. The sulfate-free formulations perform almost the same as Control A. If the lsda content is substantially lowered and silicate and sulfate are both increased, the detergency will be dramatically decreased. Sodium sulfate appears to function here as a diluent rather than a builder. An lsda level in the formulation below 15 percent does not give satisfactory results according to this test method.

Multiwash Detergency

The most promising formulations of ternary soap-sulfobetaine-silicate systems and quaternary soap-sulfobetaine-silicate-sodium sulfate systems were evaluated further according to the multiwash test developed by Schwartz and Berch (16). The results are given in Table IV. The technique involves soiling and washing the fabric six successive times and determining the amount of soiling or grayness build-up remaining after the sixth wash. The soiling data represent a decrease in reflectance ($-\Delta R$) over that of the original unsoiled fabric. In order to obtain soil redeposition data, unsoiled fabric swatches were washed along with the soiled ones. These unsoiled swatches were thus laundered six successive times, and their loss in whiteness ($-\Delta R$) due to transfer of dirt from the wash solution to the fabric was also measured and tabulated in Table IV. Both Indianhead cotton and a cotton-polyester blend with a permanent press finish were used in these tests. The previously mentioned phosphate-built detergent was used as Control A. In addition a phosphate-free detergent containing sodium carbonate and other builders sold by the same manufacturer in the Chicago area under the same brand name was used as Control B.

The results can be summarized in the following manner. All test formulations were superior in detergency to Control A and Control B within experimental error. All test formulations surpassed both controls with respect to soil redeposition.

Upon completion of the six-wash cycle multiwash test, the swatches were examined for build-up of foreign matter on the fiber with the aid of a scanning electron microscope. No visual difference was observable between Control A and the test detergent formulations. However, some build-up was seen in the case of Control B.

Biodegradability Studies

The biodegradation studies were carried out at 25°C by the Esso controlled nutrient procedure (17) in an aerobic system. In these tests, the surfactant under investigation was the sole source of carbon and energy. A sewage sludge culture from a fill and draw aerator was used as the inoculum. The course of biodegradation was followed by the measurement of carbon content remaining in centrifuged aliquot samples. Preliminary data indicate that TASB degraded quite rapidly during the first three days and thereafter degradation virtually stopped. TSB, on the other hand, degraded gradually over the 19-day test period but degradation was much less advanced than that of TASB. This points out that one must never assume that a straight chain surfactant such as the tallow-derived TSB is readily biodegradable. Presumably the TASB, being an amide of a fatty acid, is split readily and the fatty acid is metabolized rapidly while the remainder of the molecule may be more resistant to biodegradation. On the basis of the above information, TASB would certainly be the preferred lsda of this study because of its good detergency and superior biodegradability to TSB.

Summary

It has been shown that amphoteric sulfobetaines are excellent lime soap dispersing agents which can be formulated into soap-based detergent formulations. It is significant that there is substantial latitude in formulation both with respect to the soap-lsda ratio and the amounts of builders used. Sodium sulfate can be incorporated into the formulation without great detriment to performance. From the standpoint of biodegradability, an amide type of amphoteric is preferred. The soap-lsda formulations do not appear to produce large deposits on the fabric and thus would not cause appreciable modification of the fabric.

It should be pointed out that this was a preliminary investigation and the objective of this study was to establish the concept of soap-sulfobetaine detergents. The amphoterics selected may not necessarily represent the most effective or least costly ones that could be produced, and the formulations do not represent complete consumer products.

Acknowledgment

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TABLE I

ΔR Detergency Range of Soap + TSB + 10 to 50% 1:1.6 Na₂O:SiO₂ Silicate

Soap:TSB Ratio	EMPA	UST	TF
70:30	26.2-30.9	9.9-10.5	12.0-16.3
75:25	27.7-33.8	9.3-11.2	11.6-16.0
80:20	29.5-35.0	9.5-10.5	12.4-14.0
85:15	28.4-32.5	8.4-10.5	8.7-14.9
90:10	21.3-31.4	6.0- 9.1	5.9-11.1
Control A	32.9	8.6	17.8

TABLE II

Lime Soap Dispersant Requirements

Compound	LSDR (%)
TSB	3
TASB	3
TB	12
LAS	45
AOS[a]	25
TMS[b]	9

[a] Alpha-olefin sulfonate.
[b] Sodium methyl alphasulfotallowate.

TABLE III

Detergency of Three and Four Component Formulations Based on Soap and Amphoteric LSDA (at 120°F and 300 ppm Water Hardness)

% Composition				ΔR		
Soap	LSDA	Sodium Silicate	Sodium Sulfate	EMPA	UST	TF
64	21 (TSB)	15	0	35.2	13.4	23.6
51	17 (TSB)	12	20	19.7	13.0	22.8
45	15 (TSB)	10	30	17.8	13.1	22.0
60	20 (TSB)	20	0	36.1	13.8	21.3
48	16 (TSB)	16	20	31.8	13.8	19.8
42	14 (TSB)	14	30	27.9	13.9	18.6
64	21 (TASB)	15	0	35.1	12.8	18.5
51	17 (TASB)	12	20	30.0	12.2	20.8
45	15 (TASB)	10	30	27.1	12.1	15.5
68	17 (TASB)	15	0	36.5	10.9	16.5
54	14 (TASB)	12	20	25.3	9.3	15.0
48	12 (TASB)	10	30	21.4	9.4	11.4
64	21 (TB)	15	0	25.9	7.3	11.4
51	17 (TB)	12	20	17.8	6.2	8.1
45	15 (TB)	10	30	15.7	6.0	6.9
68	17 (TB)	15	0	29.0	6.3	9.9
54	14 (TB)	12	20	17.5	6.1	7.1
48	12 (TB)	10	30	12.9	5.9	6.7
Control A				39.7	11.5	24.7

TABLE IV

Multiwash Detergency and Redeposition Data

Code #	% Composition				Cotton-Polyester —ΔR		Cotton —ΔR	
	Soap	LSDA	1/1.6 Silicate	Na$_2$SO$_4$	Soiling	Redep.	Soiling	Redep.
1	64	21 (TSB)	15	0	6.1	2.6	8.5	2.6
2	45	15 (TSB)	10	30	7.5	3.4	8.7	2.7
3	64	16 (TSB)	20	0	5.5	2.5	7.8	2.7
4	45	11 (TSB)	14	30	6.8	2.9	8.4	2.8
5	64	21 (TASB)	15	0	6.4	2.9	8.3	3.4
6	45	15 (TASB)	10	30	7.5	3.0	8.5	2.8
7	64	16 (TASB)	20	0	6.8	3.6	8.3	3.2
8	45	11 (TASB)	14	30	8.2	3.3	9.0	3.2
Control A					7.7	4.9	9.9	4.5
Control B					10.0	5.2	14.6	6.5